THE SYNTHESIS OF VINYL ALCOHOLS FROM ENOL PEROXIDES AND FROM KETENES

BY

WILBUR JAY SHENK, JR.

A. B., Princeton University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

A number of stable hydrocarbon derivatives of vinyl alcohol, both ketone enols[1,2,3] and aldehyde enols,[4,5,6] are well known. In the present work effort was directed chiefly to the problem of developing methods of synthesis which would make the vinyl alcohols more readily available. Also, particular attention was paid to the possibility of obtaining the aldehyde forms corresponding to stable 2,2-diarylvinyl alcohols.

Discussion of Results

Attempts to prepare mesitylphenylacetaldehyde by (1) the ketonization of mesitylphenylvinyl alcohol[7,8], (2) the Rosenmund reduction of mesitylphenylacetyl chloride[7] and (3) the catalytic reduction of mesitylphenylketene[9] have all been unsuccessful. The preparation of diphenylacetaldehyde by the thermal decomposition of 1-mesityl-3,3-diphenyl-1-propen-1-ol peroxide[10] suggested an approach to this problem.

The cleavage of 1,3-dimesityl-3-phenyl-1-propen-1-ol peroxide and 1,3,3-trimesityl-1-propen-1-ol peroxide yielded instead of the expected aldehydes, however, 2-mesityl-2- phenylvinyl alcohol and 2,2-dimesitylvinyl alcohol, respectively. These results made it seem likely that these aldehydes could not be isolated and attention was turned to the synthesis of other aldehydes whose enol forms might also be stable. 3,5-Dibromomesitylphenylacetaldehyde was given particular consideration as it has been shown that the introduction of bromine atoms into the mesityl nucleus markedly alters its properties.[11,12] 1,3-Dimesityl-3-cyclohexyl-1-propen-1-ol peroxide and 1,3-di(3,5-dibromomesityl)-1-buten-1-ol peroxide were prepared.

The preparation of unstable triphenylvinyl alcohol from diphenylketene and phenylmagnesium bromide by Gilman and Heckert[13] suggested that the condensation of properly substituted ketenes with appropriate Grignard reagents would yield stable

vinyl alcohols. This approach was investigated first by Armstrong[9] who obtained 1-mesityl-1-phenylpropanone from mesitylphenylketene and methylmagnesium iodide.

When mesitylphenylketene, which was prepared by the procedure of Kneisley[14] (mandelic acid → mesitylphenylacetic acid → mesitylphenylketene), was condensed with mesitylmagnesium bromide and the resulting enolate solution was poured into an ice-hydrochloric acid mixture, the stable vinyl alcohol, 1,2-dimesityl-2-phenylvinyl alcohol, m.p. 140°, was liberated. Decomposition of the enolate solution with acetyl chloride yielded an acetate, m.p. 180°. α-Phenyldesoxymesitoin, m.p. 164°, the ketone corresponding to this vinyl alcohol, was prepared from mesitylphenylacetyl chloride and mesitylmagnesium bromide and from chlorophenacetyl chloride, mesitylene and aluminum chloride. It was converted to the enol by boiling with sodium ethoxide and to a new acetate, m.p. 161°, by the action of methylmagnesium iodide (under forcing conditions) followed by acetyl chloride. Both acetates gave, upon hydrolysis, the same form of the vinyl alcohol, m.p. 140°. Acetylation of the vinyl alcohol with acetic anhydride in the presence of pyridine produced the low-melting acetate. Evidently during the hydrolysis one form of the vinyl alcohol underwent a direct *cis-trans* isomerisation. Infra-red absorption spectrum measurements, for which the author is indebted to Prof. W. H. Rodebush and Mr. R. M. Whitney, verified the simple keto-enol relationship.

Treatment of mesitylphenylketene with phenylmagnesium bromide produced 2-mesityl-1,2-diphenylvinyl alcohol which was stable for some time in cold solution, as evidenced by peroxide formation, but yielded α-mesityldesoxybenzoin when attempts were made to isolate it. This ketone readily formed an acetate when boiled with acetic anhydride and pyridine (evidence of the ready interconvertibility of the ketone and the unstable enol) and was reduced by isopropylmagnesium bromide to 2-mesityl-1,2-diphenylethanol which was isolated as the acetate. The structure of the ketone was confirmed by an independent synthesis, which involved condensation of desyl chloride with mesitylene, and by infra-red absorption spectrum measurements.

When mesitylphenylketene was treated with cyclohexylmag-

nesium chloride, reduction rather than addition occurred, and an 80 per cent yield of 2-mesityl-2-phenylvinyl alcohol was obtained.

Free 2,4,6-triisopropylphenylketene was not obtained by the method of Schroeter:[15] 2,4,6-triisopropylphenylglyoxal monohydrazone → 2,4,6-triisopropylbenzoyldiazomethane → 2,4,6-triisopropylphenylketene; but 2,4,6-triisopropylphenylacetic acid was prepared by the decomposition of the diazomethane in boiling water.

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Vita

The author was born in Erie, Pennsylvania, on November 3, 1918. He attended the public schools of Cleveland, Ohio and was graduated from the University School in June, 1936. The following June he was graduated from Phillips Exeter Academy. He entered Princeton University the same year and was granted the Bachelor of Arts degree in June, 1941. He was employed as a research assistant by the Harshaw Chemical Company during the summer of 1941. That autumn he entered the University of Illinois where he held a teaching assistantship until February, 1944. During the spring semester of 1943-44 he was a special research assistant in chemistry.

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